California Environmental Protection Agency

Air Resources Board

SOP MLD061

STANDARD OPERATING PROCEDURE (SOP) FOR THE TRACE ELEMENTAL ANALYSIS OF LOW-VOLUME SAMPLES USING INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY (ICP-MS)

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Monitoring and Laboratory Division (MLD)

Date SOP for MLD061 First Approved: May 1, 2002
Revision Number: 0.0

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STANDARD OPERATING PROCEDURE (SOP) FOR THE TRACE ELEMENTAL ANALYSIS OF LOW-VOLUME AMBIENT AIR SAMPLES USING INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY (ICP-MS)

1. SCOPE

This document details the acid extraction and trace elemental analysis of ambient air samples using an inductively coupled plasma-mass spectrometer (ICP-MS). The extraction procedures herein are suitable for low-volume ambient air samples collected on exposed Teflon membranes, sized up to 47 millimeters in diameter. Also, this document outlines the basic steps necessary to develop an analysis method for other types of air samples requiring trace metal analysis by ICP-MS.

1.1 Northern Laboratory Branch (NLB) uses the acronym ICP-MS as designated by the instrument manufacturer(s) and patent holder(s) of this technology. The United States Environmental Protection Agency (U.S. EPA) alternately uses the acronyms ICP-MS and ICP/MS. Literature searches should include both acronyms.

1.2 ICP-MS offers improved detection limits over previous elemental analysis techniques, which is essential given the decreasing levels of toxic metals found in ambient air. Also, ICP-MS allows for the rapid determination of a multitude of isotopic analytes previously uncharacterized by the Air Resources Board (ARB).

1.3 This method gives the basic procedures for preparing sample extracts, analyzing the extracts, and determining the reliability of the data acquired. Since sample matrices and analytes of interest both fluctuate, the analyst is responsible for demonstrating the accuracy and precision of the method by monitoring potential sources of interferences and taking appropriate action to ensure data of known quality. The analyst using this method should be knowledgeable in the recognition and correction of spectral, chemical and physical interferences in ICP-MS.

2. DEFINITIONS

2.1 **Inductively Coupled Plasma-Mass Spectrometer.** An analytical instrument that uses a radio-frequency inductively coupled plasma (ICP), which nebulizes (aerosolizes) a liquid sample into a state of ionization, configured in series with a quadropole mass spectrometer (MS), which separates the resulting ions by their mass-to-charge ratios, and then quantifies the number of ions detected using an electron multiplier detector. Interferences, mass-to-charge ratio overlaps, and background ions must be assessed and valid corrections applied. (Figure 18.1)

2.2 **Limit of Detection (LOD).** A calculated value that represents the minimum concentration of an analyte that can be reported with 99% confidence. (Section 17)

2.3 Ultrasonic Nebulizer / Desolvator. A two-fold device that: 1) uses transducer-based sonication to convert liquid samples into aerosols prior to being introduced into the plasma for ionization; and, 2) heats, then cools the nebulized sample to remove much of the primary solvent, which for this method is water. The desolvator lessens the interference effects of hydrogen and oxygen. (Figure 18.2)

3. SUMMARY OF METHOD

3.1 Ambient air particulates, collected on Teflon membranes, are extracted into a dilute nitric acid solution by sonication with heating. The extraction solution is stored at room temperature until elemental analysis by ICP-MS.

3.2 This method uses an ultrasonic nebulizer serially configured with a desolvator unit. If a pneumatic nebulizer is used, additional correction equations for hydrides, oxides, and dioxides must be added.

3.3 This method is known to be suitable for $PM_{2.5}$, Dichotomous PM_{10} (Dichot), and Total Metal samples, provided the particulates are collected on Teflon membranes. Depending on the analytes of interest, this method may not be suitable for analysis of air samples collected on quartz or glass micro-fiber filters.

3.4 For special projects, the analyst should request that air volumes be high enough that the liquid volumes necessary for extraction allow for analysis using the ultrasonic nebulizer. If the sampling air volume cannot be increased, the analyst can reduce the instrument sweeping parameters or use a less effective nebulizer, such as the crosscut pneumatic, which will require the need for additional correction equations for oxides and hydrides.

4. LABORATORY INTERFERENCES

4.1 Contamination of samples will be less likely if the analyst does:

4.1.1 Wear talc-free gloves when handling unexposed or exposed filters.

4.1.2 Clean all equipment used in the sample preparation and analysis in a manner consistent with good laboratory practices for metals analysis.

4.1.3 Use American Society for Testing and Materials (ASTM) Type I de-ionized (DI) water, with a resistivity of greater than 17.8 megaohms, for sample extraction and standard preparation. Record the resistivity prior to use. Back rinse the end of the delivery tube before filling containment vessels.

5. CHEMICAL INTERFERENCES

5.1 Pay close attention to the nature of solutions introduced to the ICP-MS.

5.1.1 Nitric acid at less than 2% (v/v) is required for ICP-MS analysis to minimize the damage to the interface and to minimize isobaric molecular interferences (Section 6.1).

5.1.2 In general, when developing an analysis method, try to use a final nitric acid concentration of 1% for all analysis solutions. If higher acid extractions are required, dilute to 1% to minimize formation of nitrates.

5.1.3 The final dilutions of sample extracts must match the acid content of the calibration standards in order to match potential interferences.

5.1.4 The concentration of dissolved solids in analysis solutions should be less than 2% because of the sample interface on the instrument. Higher concentrations may plug the sample cone orifice.

5.1.5 Precautions must be taken to protect the channel electron multiplier from high chemical concentrations (high ion currents). The channel electron multiplier suffers from fatigue after being exposed to high ion currents. This fatigue can last from several seconds to hours depending on the extent of exposure. During this period, response factors are constantly changing, which causes instrument instability that invalidates the calibration curve, and, thereby, invalidates all associated sample results. A sodium bicarbonate ($NaHCO_3$) sample matrix is known to cause this problem.

6. INSTRUMENT INTERFERENCES

6.1 Isobaric Molecular and Doubly-Charged Ion Interferences

Proper correction of isobaric molecular and doubly-charged ion interferences is fundamental to successful analysis using ICP-MS. Therefore, it is recommended that the analyst consult sources beyond this SOP for further details on correcting for these interferences. The Perkin-Elmer ICP-MS instrument manual goes over how to develop correction equations for molecular interferences, and how to insert the equations into the electronic method. When troubleshooting interferences, it is safe to assume that all isobaric and doubly-charged interferences that could affect ICP-MS determinations have already been identified in the literature.

6.1.1 Isobaric molecular interferences are caused by ions consisting of more than one atom. For example, the contribution of ArCl on the ^{75}As signal.

6.1.2 Doubly-charged ion interferences are caused by ions consisting of more than one charge. For example, the contribution of MoO^{+} ions on the Cd isotopes.

6.2 Spectral Interferences

A spectral interference results from the presence of other isotopes or ions that have the same atomic weight or mass number as the analyte.

6.2.1 For single isotope interferences, such as the effect of ^{54}Fe on ^{54}Cr, the Perkin-Elmer software (version 2.3.2) automatically gives starting point suggestions for correction equations. For the numerous multi-element interferences (compounds), the analyst will need to determine the correction equations.

6.2.2 Very high ion currents at adjacent masses can contribute to ion signals at the mass of interest. Although this type of interference is uncommon when analyzing samples solutions from Teflon membranes, it can be a problem for other types of samples, such as those collected on quartz or glass micro-fiber filters. Correction of these types of problems could require resolution improvement, matrix separation, analysis using another isotope, or a different method.

6.2.3 Isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z) cause isobaric elemental interferences. Correction of these interferences involves calculating the signal of the interference element, by using its natural abundance ratio with another of its isotope(s), and then subtracting the calculated signal of the interference from the total signal of the analyte isotope.

6.3 Transport Interferences

Transport interferences are a specific physical interference associated with the sample nebulization and transport process through the instrument. These usually result from sample matrix components that influence the aerosol formation or cause a change in the surface tension or viscosity. Changes in the matrix composition can cause observed signal suppression or enhancement.

6.4 Matrix Interferences

Matrix interferences are caused by the elemental properties of the samples in solution. To identify matrix interferences, determine if the response is linear by diluting the sample, and then perform analyses at varying low and high nebulizer argon flow rates.

6.4.1 For matrices of known composition, match the composition of the standards to that of the samples.

6.4.2 For matrices of unknown composition, use an internal standard (Section 9.3) that has been matched to the analyte so that the two elements are similarly affected by matrix changes.

6.5 Memory Interferences

Memory interferences can occur when there are large concentration differences between samples or standards that are analyzed sequentially. Sample deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer all affect the extent of the memory interferences that are observed. The rinse period between samples must be long enough to eliminate significant memory interference.

7. APPARATUS AND MATERIALS

7.1 Inductively coupled plasma-mass spectrometer

7.2 Peristaltic pumping system capable of circulating at least four solutions

7.3 Ultrasonic Nebulizer configured with a desolvator

7.4 Sample vials, polypropylene, equipped with screw-top caps

7.5 Sonication bath with heating capability to 69 degrees Celsius (°C)

7.6 Quartz heating rod, used if needed to supplement the heating capability of the sonication bath

7.7 Micro-pipettes with metal-free disposable tips, 100-microliter (µl) to 10-milliliter (ml) capacity

7.8 Miscellaneous: talc-free gloves; disposable laboratory wipes/towels; self-adhesive labels; waterproof ink pen; timer

8. REAGENTS

8.1 Nitric Acid, concentrated, spectrophotometric grade, ultrapure

8.2 De-ionized water, ASTM Type I, filtered, with a resistivity of greater than 17.8 megaohms

8.3 Argon gas, high purity grade (99.99%); tanks allow for longer runs, and are recommended over cylinders

8.4 ICP-MS Grade Reference Standards, National Institute of Standards and Technology (NIST) traceable material, 10 μg/ml stock, in two percent nitric acid; diluted to make necessary analysis solutions

8.5 Secondary source of Reference Standards

8.6 Ethanol, spectrometric grade, for use with the alternative extraction procedure

9. ANALYSIS SOLUTIONS

9.1 Calibration Standards

9.1.1 Concentrations of the calibration standards chosen should be within the linear range for each element. To avoid precipitation problems and short storage-life, be sure that the elements used in the calibration standard dilutions are compatible. Use a chemical reference to verify compatibility; failure to do so may result in unwanted precipitates.

9.1.2 Calibration standards must be verified using a quality control standard (Section 9.2) and monitored closely for stability.

9.2 Control Standard

The control standard is the initial calibration verification solution that must be prepared in the same acid matrix as the calibration standards. This solution must be an independent standard near the midpoint of the linear range at a concentration other than that used for the instrument calibration. An independent standard is defined as a standard composed of the analytes from a source different from those used in the standards for instrument calibration.

9.3 Internal Standard

Selecting the proper internal standard, at an ideal concentration, can eliminate the need for some correction equations.

9.3.1 The internal standard should be no more than 50 atomic mass units (amu) removed from the analyte.

9.3.2 Recommended internal standards for this method are ^{45}Sc, ^{69}Ga, ^{89}Y, ^{115}In, and ^{209}Bi for analytes beginning with Mass 23 and ending with Mass 238.

9.3.3 To cover a lower mass range, use ^{6}Li.

9.3.4 Depending on the behavior of the analyte(s) of interest for a given matrix, the analyst should alternately try ^{103}Rh, ^{159}Tb, and ^{169}Ho.

9.3.5 For sample types not specifically listed in this method, the analyst should test alternative internal standards.

9.3.6 Concentration(s) of the internal standard(s) for this method should be 5 to 50 nanogram per milliliter (ng/ml).

9.3.7 The concentrations should be selected based on interference correction needs. Select a high enough concentration that normal shift(s) in the sample matrices are made inconsequential.

9.3.8 Unnecessarily high internal standard concentrations will contribute to detector fatigue (Section 5.1.5).

9.3.9 For method development, the concentration may need to exceed 50 ng/ml. A concentration of 200 ng/ml is not unreasonable, especially for the crosscut nebulizer.

9.3.10 Internal standards may be added in-line at the time of analysis using a channel of the peristaltic pump and an appropriate mixing manifold, or may be added manually to the calibration standards and samples.

9.3.11 Before preparing the mixed internal standard, each stock solution must be analyzed separately to determine possible spectral interferences (Section 6.2) or the presence of impurities. Mixed internal standards must be prepared as needed with the realization that concentrations can change on aging.

9.3.12 The concentration of internal standard must be added equally to the reagent blank, to the calibration standards, and to the samples.

9.4 Tuning Solution

The tuning solution usually contains elements representing all of the mass regions of interest, thereby verifying that the resolution and mass calibration of the instrument are within the required specifications (Section 15.7). The solution is also used to verify that the instrument has reached thermal stability.

9.4.1 The tuning solution used for this method is 5 ng/ml Li, Co, Ce, In, Bi in 1% nitric acid.

9.4.2 Only include analytes in this solution that are actually in the tuning method.

9.4.3 When analyzing for a single analyte at a low concentration, narrow the tuning mass range significantly. Include the isotope of interest as well as the internal standard. For example, when analyzing for ^{52}Cr, include its

internal standard, ^{69}Ga, in the tuning solution. When testing for a specific analyte isotope, it may be suitable to include a second isotope of the same analyte.

9.4.4 In general and for method development, always extend the tuning range beyond the range of interest.

9.5 Pulse Detector Solution

The pulse detector solution is used when performing a pulse stage detector optimization.

9.5.1 The solution should contain 5 ng/ml In or other suitable element, such as Rh, depending on the analytes of interest. Prepare using a 1% nitric acid matrix.

9.5.2 To reduce the time needed to optimize, the method should have a single analyte.

9.6 Analog Detector Solution

The analog solution is used when performing an analog stage detector optimization. Use a high calibration standard solution when possible.

9.6.1 The solution should contain 50 ng/ml Mg or other suitable element, depending on the analytes of interest. Prepare using a 1% nitric acid matrix.

9.6.2 To reduce the time needed to optimize, the method used for this should have only a single analyte.

9.7 Optimization Solution

The optimization solution is used when performing the daily optimization procedures (Table 1).

9.7.1 Ideally, the solution should contain the analytes needed to do a lens calibration and a pulse detector calibration.

9.7.2 At a minimum, all analytes in the optimization solution should be needed in the lens calibration and pulse detector calibration.

9.7.3 For this method, use the analytes of interest at a concentration of 5 ng/ml in 1% nitric acid.

9.8 Performance Check Solution

The performance check solution is used when checking the instrument performance as part of the daily optimization procedures (Table 1). The solution used is 5 ng/ml Li, Co, Ce, In, Bi in 1% nitric acid.

9.9 Dual Detector Calibration Solution

The solution should contain the same elements as in the calibration standard solutions at a concentration of 50 ng/ml in 1% nitric acid.

9.10 Interference Check Solution (ICS)

The ICS is intended to evaluate corrections for known interferences on analytes. An ICS should be prepared containing known concentrations of interfering elements to demonstrate the magnitude of the interferences and provide an adequate test of any corrections. The ICS is used to verify that the interference levels are corrected within quality control limits (Section 17.4) by the data system. Use either a commercially prepared mixture or prepare limited mixtures to target possible problems for a given matrix. Some examples:

9.10.1 Chloride in the ICS provides a means to evaluate software corrections for chloride-related interferences such as $^{35}Cl^{16}O^{+}$ on $^{51}V^{+}$ and $^{40}Ar^{35}Cl^{+}$ on ^{75}As.

9.10.2 Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese.

9.10.3 Molybdenum serves to indicate oxide effects on cadmium isotopes.

9.10.4 Add other components to the ICS to evaluate the ability of the measurement system to correct for various molecular-ion interferences.

10. BLANKS

There are at least three types of blanks required for the analysis: the calibration blank, the rinse blank, and the extraction (method) blank. Below is a discussion about each.

10.1 Calibration Blank (Reagent Blank)

The calibration blank is used in establishing the calibration curve before analysis of samples. It should be a solution of 1% nitric acid and include the exact internal standard that will be a part of the standard calibration and sample analysis. If additional components (such as hydrochloric acid) are needed for stability of some analytes, then the additional components must be included in the calibration blank. The same solution is used to verify contamination during analysis. Analyze the

solution prior to analyzing a sample batch (pre-analysis) and after analyzing the same sample batch (post-analysis). The batch should be re-analyzed if either result is found to be greater than the LOD for any reported analyte.

10.2 Rinse Blank

The rinse blank is used to flush the system between all samples and standards. Plain de-ionized water may be suitable, based on the Reagent Blank results. The rinse blank should consist of no more than 1% nitric acid for the rinse cycle between samples. Increase to no more than 2% acid for cleaning purposes, and do not run for prolonged periods.

10.3 Extraction Blank (Unexposed Filter Blank)

The extraction blank is carried through the complete sample preparation procedure. The extraction blank contains a Teflon filter (unexposed) and the same volumes of reagents as the sample solutions.

11. SAMPLE PREPARATION OF LOW-VOLUME AIR SAMPLES COLLECTED ON TEFLON FILTERS (37-MILLIMETERS IN DIAMETER)

11.1 Prepare sample labels using a waterproof pen. On each label, write at a minimum the sample identification number and the date of the extraction. Method blanks using unexposed filters kept in the laboratory should be labeled to distinguish them from other types of blanks, e.g. Trip Blanks, brought in from the field.

11.2 For each sample to be extracted, use a clean, metal-free extraction vial. For best results, affix each label to the cap of the extraction vial. The labels should adhere confidently. Loose labels will come off in the sonicator.

11.3 Wash and rinse a two-liter amber glass bottle fitted with an adjustable dispensing unit. Fill this bottle with 4% nitric acid. Adjust the dispenser to deliver 16-ml aliquots; verify dispensed volume by weight (consider the dilute acid solution to be the same density as pure water).

11.4 Repeat the following steps (Sections 11.4.1 through 11.4.5) for each sample listed on the extraction worklist:

11.4.1 Place each 37-mm Teflon filter into a separate, labeled extraction vial, being sure that the filter is as far down in the vial as possible (Figure 11.4.1).

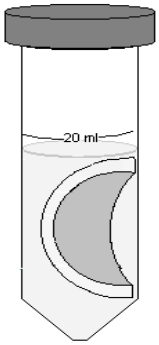

Figure 11.4.1, Extraction Vial Set-Up

11.4.2 If the filter is properly positioned in a 50-ml centrifuge tube, a volume of 16 ml should cover the exposed portion of the filter. In some cases, a slender portion of the filter may be left above the solution level.

11.4.3 Failure to position the filter as indicated may cause the filter to float and yield incomplete sample extraction.

11.4.4 The position of the filter(s) should be checked periodically during sonication. On occasion, be prepared to use a clean glass rod to push a floating filter back into the solution.

11.4.5 Dispense a 16-ml aliquot of 4% nitric acid into the vial with the filter. Seal the vial with a cap and place in a rack.

11.4.6 For special projects, adjust the amount of acid added based on the analytes of interests. A lower volume, such as 16 ml is good to target low concentration elements, such as Cr. Increase volume to keep high concentration elements, such as Fe, within the linear range of the instrument. Whatever volume is used, be certain the acid covers the entire filter.

11.4.7 Make sure to adjust the final calculation to reflect the actual volume used.

11.4.8 The same procedure should be followed for the preparation of a method blank, using a clean, unused Teflon filter.

11.5 Place the filled racks, two to three centimeters apart in the sonication bath. Plug in the heating rod first, then insert it into the sonication bath, taking care not to allow the rod to touch the extraction vial racks or the sides of the sonication unit. The heated portion of the heating rod, which operates at 900 degrees Celsius (^{o}C), will melt most anything solid that touches it.

11.6 The samples should be sonicated for three full hours with the sonicator set to a temperature of 69 ^{o}C. Follow the manufacturer's suggestions for effective operation of the sonication bath.

11.7 After the samples and blanks have finished sonicating, allow the solutions to cool to room temperature. The extraction solutions are then ready for dilution to 1% nitric acid and subsequent analysis by ICP-MS.

12. SAMPLE PREPARATION OF LOW-VOLUME AIR SAMPLES COLLECTED ON TEFLON FILTERS (47-MILLIMETERS IN DIAMETER)

12.1 Follow all procedures listed in Section 11, except increase the volume of 4% nitric acid used (Section 11.4.5) from 16 ml to 32 ml or greater. Adjust the final nitric acid concentration to 1% prior to analysis by ICP-MS.

12.1.1 $PM_{2.5}$ samples are collected on 47-mm Teflon filters

13. ALTERNATE PROCEDURE FOR SAMPLE PREPARATION

This alternate procedure may provide better recoveries for some analytes, and also eliminates the manual dilutions required of 4% nitric acid samples.

Keep in mind that the addition of even small amounts of ethanol will significantly alter the intensities. Carbon bonding can greatly increase spectral interferences, and, in doing so, greatly decrease the intensities of particular analytes involved in C-X bonding. This alternate procedure is known to significantly dampen the intensities detected for As and Cu, and to entirely hamper the detection of all of the K isotopes.

13.1 After positioning the filter in the extraction file, moisten the membrane with ethanol. Use 50- to 150-µl, depending on the size of the membrane. Take care to cover the entire exposed area of the membrane with the aliquot of ethanol. Use the smallest aliquot volume possible to consistently wet the membrane, and use the same aliquot volume for every sample in a given project.

13.1.1 Teflon is a hydrophobic material. The extraction solution will not penetrate the membrane unless the hydrophobic nature of Teflon is eliminated using a solvent, such as ethanol (spectrometric grade).

13.2 Repeat the steps in Section 11 for each sample.

13.3 Adjust the calibration standards to include the same amount (v/v) of ethanol as the samples.

14. DAILY OPTIMIZATION

The following optimization procedures should be performed daily, even if the previous analysis was for samples of similar matrices. The instrument must run for at least fifteen minutes with the plasma on before optimization. The information provided below is not intended to replace the operator's manual.

14.1 Perform X-Y Adjustment

14.1.1 The X-Y adjustment needs to be performed whenever the sample or skimmer cones are changed, or whenever the plasma torch has been removed or its configuration altered.

14.1.2 Using the optimization solution rotate the X and Y adjustment knobs to obtain the positions resulting in the maximum signal intensities. It seems to work best if the Y adjustment is done first. Repeat the adjustment of each knob three times or until the best signal intensity is achieved.

14.2 Perform nebulizer gas flow optimization

14.2.1 Perform this optimization while observing a signal from one of the optimization solution analytes.

14.2.2 The curve should increase, attain a maximum point, and then decrease (appearing like a mountain). If the curve is not satisfactory, adjust the Start and End values in the Parameter Range fields and repeat optimization.

14.2.3 To reduce analyte oxide levels, follow the operator's manual instructions for reducing the nebulizer gas flow.

14.3 Perform lens optimization

14.3.1 Use the optimization solution. The software will perform the optimization and then automatically set the lens voltage to the optimum value when the procedure is complete.

14.3.2 Flush the sample introductory system with reagent water when the optimization is complete.

14.4 Check instrument performance

14.4.1 Use the Performance Check Solution.

14.4.2 The performance specifications when using the ultrasonic nebulizer are:

Background:	<80 cps at Mass 220
CeO / Ce:	≤ 0.0004
Ce^{++} / Ce:	≤ 0.01
In Sensitivity:	>150,000 cps

14.4.3 When troubleshooting performance problems, it may be necessary to use the crosscut pneumatic nebulizer. Typical performance specifications using the crosscut are:

Background:	<30 cps at Mass 220
CeO / Ce:	≤ 0.03
Ce^{++} / Ce:	≤ 0.05
In Sensitivity:	>75,000 cps

14.4.4 If the performance check is satisfactory, flush the system with DI water and begin the analysis.

14.4.5 If the performance check is not satisfactory, check the conditions of the peristaltic pump tubing, the cones, and check the position and cleanliness of the torch and injector. Once this inspection is complete, repeat each of the daily optimization procedures.

15. COMPLETE OPTIMIZATION

The following optimization procedures should be performed every 2 weeks, or whenever the sample background matrix changes significantly. Perform the detector optimization (Sections 15.1 and 15.2) in the following order: Pulse, Analog, repeat Pulse, repeat Analog, then perform a Daily Optimization (Section 14) in addition to these procedures.

15.1 Pulse Stage Detector Optimization

15.1.1 Use the pulse detector solution.

15.1.2 The software performs the optimization. A plot of intensity versus pulse stage voltage will be displayed. A diamond indicates the optimum point.

15.2 Analog Stage Detector Optimization

15.2.1 Use the analog detector solution.

15.3 Dead Time Correction

15.3.1 Dead time (τ) is the amount of time required for the detector and its associated electronics to process the signal from an incident ion. After

an ion strikes the detector it will not be able to record another ion strike until a time, τ, has elapsed. The detector is "dead" for τ seconds (typically 50- to 60-nanoseconds).

15.3.2 This procedure need only be done as part of the complete optimization procedure.

15.3.3 Use the dead time correction value that results in the highest correlation coefficient (typically 0.9999).

15.4 Dual Detector Calibration

15.4.1 Use the dual detector calibration solution.

15.4.2 Prior to performing this procedure, the analog and pulse stages of the detector must first be calibrated.

15.4.3 Dual detector calibration is used to extend the dynamic range of the detector by normalizing the analog stage of the detector to the pulse stage.

15.5 Lens Calibration

15.5.1 Use the optimization solution for this procedure.

15.5.2 This procedure is done only after all prior optimization procedures have been performed.

15.6 Check Oxides, Doubly-Charged Ions, Background and Sensitivity

15.6.1 Use the tuning solution to perform this procedure.

15.6.2 All prior optimization procedures must be complete before performing this procedure. Compare values obtained with those listed in Section 14.4.3.

15.7 Perform Mass Calibration and Resolution Check

The mass calibration step should only be performed after attaining satisfactory results from the instrument performance check (Section 14.4).

15.7.1 Use the tuning solution to verify the resolution and mass calibration of the instrument.

15.7.2 Conduct the mass calibration and resolution checks in the mass regions of interest.

15.7.3 The mass calibration and resolution parameters are required criteria that must be met prior to analysis of samples. If the mass calibration differs more than 0.05 amu from the true value, then the mass calibration must be adjusted to the correct value.

15.7.4 The resolution must also be verified to be within 0.1 amu of the target value. The DAC value should be 0.65 at 10% peak height, as suggested by Perkin-Elmer service. The Perkin-Elmer manual gives a DAC target of 0.7 at 10% peak height. Be consistent with whatever target value is chosen.

16. SAMPLE ANALYSIS

16.1 Refer to Section 17 and Table 2 for a description of quality control measures required for this method. The analyst should follow the manufacturer's instructions for safe operation of the instrument. Allow at least 30 minutes for the instrument to equilibrate before analyzing any samples.

16.2 Verify instrument performance by analyzing the tuning solution at least four times with relative standard deviations of less than or equal to five percent for the analytes contained in the tuning solution.

16.2.1 If the standard deviations exceed five percent, check the X-Y adjustment, the argon flow on the nebulizer, the ICP-MS plasma flow, and the condition and position of the torch, the skimmer and sampling cones prior to trying a re-make of the tuning solution.

16.2.2 If the tactics listed above do not improve performance, then run a complete optimization.

16.3 Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run or once every twelve hours, whichever is more frequent. This is done by either analyzing the interference check solution or by analyzing the control solution.

16.3.1 The analyst should be aware that precipitation might occur with some elements, specifically silver. Refer to Section 6 for a discussion on the interferences and the literature for potential solutions to those interferences if additional guidance is needed.

16.4 Calibrate the Instrument

16.4.1 Calibrate for the analytes of interest using a calibration blank and at least three calibration standards.

16.4.2 The results of the calibration blank must be less than three times the limit of detection (LOD) for each element. If this is not the case, the reason for the out-of-control condition must be identified and corrected, and affected samples re-analyzed. If the concentration of the blank is consistently greater than three times the LOD, the LOD may be indicative of an estimated LOD and should be re-evaluated.

16.4.3 Flush the system with the rinse blank between standard solutions.

16.4.4 Use the average of at least 3 integrations for both calibration and sample analysis, unless the available sample volume is limited.

16.5 Verify Calibration with the Control Standard

16.5.1 Immediately after the calibration has been established, the calibration must be verified for every analyte by the analysis of the control solution.

16.5.2 The results should be within established limits of the expected target value. If the control value is out of range, the analysis must be terminated, the problem corrected, the instrument recalibrated and the new calibration verified. The instrument may need adjusting prior to recalibration, or the solutions may be invalid, requiring that a new set of standards and a new control be prepared.

16.5.3 Any samples analyzed under an out-of-control calibration are considered invalid and must be re-analyzed.

16.5.4 During the course of an analytical run, the instrument may be resloped or recalibrated to correct for instrument drift. A recalibration must then be followed, immediately, by a new analysis of the control before any further samples may be analyzed.

16.6 Standard Check

A check of a mid-range standard should be made every ten samples and after completion of the last sample. Should a standard check be greater than $\pm$ 10% of the expected value, recalibrate and re-analyze the samples back to the point where the calibration was known to be in control.

16.7 Analyze Samples

16.7.1 The extraction blanks should be treated as samples and should be analyzed along with the ambient filter samples.

16.7.2 The system should be flushed with the rinse blank for about thirty seconds (or until the signal levels return to the method's level of quantification) before the analysis of each sample.

16.7.3 Each sample should be nebulized until a steady-state signal is achieved (usually about thirty seconds) before collecting data.

16.7.4 Samples with values greater than the linear range for an analyte must be diluted and re-analyzed, or an alternate less-abundant isotope can be measured. The linearity at the alternate mass must be confirmed by an appropriate calibration.

17. PERFORMANCE CRITERIA / QUALITY CONTROL

All quality control data should be maintained in an organized manner and be available for easy reference or inspection. Refer to Table 2 for a quick summary.

17.1 Method Limit of Detection

17.1.1 The limit of detection for each isotope is calculated according to the MLD061 reference method, EPA600/R-94-111 Method 200.8,

as follows:

$$LOD = (t)_{(n-1 = 0.99)} \times SD = 3.14 \times SD$$

where SD is the standard deviation of n repetitions of the lowest standard expressed in instrument units of ng/ml, and the $(t)_{(n-1 = 0.99)}$ is the Student's t value for a 99% confidence level and a SD estimate with a degree of freedom equal to n-1. For 7 replicates, the t value equals 3.14.

17.1.2 The y-intercept for each linear calibration must be set to zero.

17.1.3 For a method LOD, use the internal standards and the exact instrument settings (sweeps and dwell) used to analyze the ambient samples.

17.1.4 Repeat the LOD determination a minimum of 5 times, each time on a different day. Use this added information, specifically the fluctuation of results, to assist in setting the final LOD value reported for each analyte.

17.1.5 The published method LOD in aerometric units of nanogram per cubic meter (ng/m^3) must be set after the calculated values in ng/ml are evaluated by the analyst based on the analytical tendencies of actual ambient samples. Judgment as to the conversion of the calculated LOD (ng/ml) into the published LOD (ng/m^3) may be necessary, especially if the air volumes are vastly different within a sample set or project.

17.1.6 For sample types analyzed on a limited or one-time basis, it may not be possible to establish a method LOD over several days. At a minimum, run 7 replicates of the lowest standard, and use the cumulative standard deviations of the actual samples analyzed as guides to setting an LOD for the special study method.

17.2 Verifying the Method LOD

The published method LOD should be verified no less than once per year.

17.2.1 Verification of the method LOD should yield a value less than the reported LOD value.

17.2.2 If the verified value is higher than the reported value, the cause should be investigated. It may be necessary to evaluate sample data obtained after the last valid LOD verification.

17.3 Instrument Detection Limit (IDL)

The IDL is used to compare instrument to instrument functioning, or to verify manufacturer's reported values. Although NLB does not use IDL in data QC evaluations, the IDL can be useful in testing literature methods.

17.3.1 To determine an IDL, use settings for sweeps and dwell time that are unrealistic for normal analysis, but will yield the most outstanding results.

17.3.2 All consumables, in particular cones and tubing, should be new.

17.3.3 Run 7 replicates of a blank solution and a low standard. Insert the standard deviation value into the LOD equation above (Section 17.1.1).

17.4 Control Standard

The control standard is prepared using a stock source secondary to the stock source used to prepare the calibration standards.

17.4.1 Without a history of ICP-MS analysis, the control and warning limits for a quantitative method have been initially set at ±10% and ±5% of the target value for each analyte, respectively. In time, these limits will be set based on the standard deviations of the recorded mean.

17.4.2 Document each control value as a percent ratio of the actual value over the target value.

17.5 Standard Checks

At pre-set intervals during a batch analysis, the calibration must be verified using a mid-range standard or the control standard. Results must be ±10% of the target value for each analyte to verify that the calibration in use is valid. If a standard check exceeds the limit, the analysis must be stopped and the instrument must either be recalibrated or have the existing calibration(s) resloped by re-analysis of one or more of the standards. All reportable results must be re-analyzed or reprocessed with a valid calibration.

17.5.1 Document each standard check value as a percent ratio of the actual value over the target value.

17.5.2 Reprocessed data must include reprocessing of all QC samples associated with the reprocessed sample results.

17.6 Internal Standards

The intensities of all internal standards must be monitored for every analysis. When the intensity of any internal standard fails to register between 60 to 140% of the intensity of that internal standard in the initial calibration standard, the following procedure is followed:

17.6.1 The sample must be diluted fivefold and re-analyzed with the addition of appropriate amounts of internal standards.

17.6.2 Repeat dilution until the internal standard intensities fall within the prescribed window.

17.6.3 Check that the intensity levels of the internal standards for the calibration blank and interference check standard agree within ±20% of the intensity level of the internal standard of the original calibration solution. If they do not agree, stop the analysis, find and correct the problem, recalibrate, verify the new calibration, and re-analyze the affected samples.

17.7 Interferences

If the concentrations of interference sources (such as C, Cl, etc.) are such that the analyte is less than the limit of quantification and the concentration of the interferences are insignificant, then the data may go uncorrected.

17.7.1 To obtain analyte data of known quality, it is necessary to measure more than the analytes of interest to apply corrections or to determine whether interference corrections are necessary.

17.7.2 Monitoring interference sources does not necessarily require monitoring the interference itself, but that a molecular species may be monitored to indicate the presence of the interference.

17.7.3 When correction equations are used, all QC criteria must also be met. Extensive QC for interference corrections are required at all times.

17.7.4 The monitored masses must include those elements whose hydrogen, oxygen, hydroxyl, chlorine, nitrogen, carbon and sulfur molecular ions could affect the analytes of interest.

17.7.5 Unsuspected interferences may be detected by adding pure major matrix components to a sample to observe any impact on the analyte signals. When an interference source is present, the sample elements impacted must be flagged to indicate the percentage interference correction applied to the data or an uncorrected interference by virtue of the elemental equation used for quantitation.

17.7.6 The isotope proportions for an element or molecular ion cluster provides information useful for quality assurance.

17.7.7 Only isobaric elemental, molecular, and doubly-charged interference corrections which use the observed isotopic-response ratios, or parent-to-oxide ratios, are acceptable corrections for use in MLD061.

17.8 Dilution Test

If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 times greater than the concentration in the reagent blank), analysis of a fivefold dilution must agree within ± 10% of the original determination. If it does not agree within these limitations, an interference effect must be suspected.

17.9 Duplicates

If there is enough sample solution available, every tenth sample should be analyzed in duplicate as a record of the method precision.

The percent relative difference (%RD) between duplicate determinations is calculated as follows:

$$\%RD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100$$

where D_1 and D2 equal the concentrations determined for the first and second aliquots, respectively. A value of 30% RD should not be exceeded for analyte

values greater than 5 times the LOD. If this limit is exceeded, the reason must be investigated, the cause corrected if possible, and any samples analyzed during the out-of-limit conditions must be re-analyzed.

17.10 Blanks

Results for the blanks must be less than the LOD for each analyte reported. If blank value(s) exceed the LOD, the sample preparation and analysis procedures should be reviewed to determine the extent and source of contamination.

17.11 Spikes (Post-Digestion)

Post-digestion spikes are added to an aliquot of a prepared sample or its dilution. Spikes are fundamental in assuring the reliability of the method parameters and, subsequently, the data generated. The spike should be recovered within 80–120% of the known value, based on the original concentration of each element of interest in the sample.

The percent recovery (%R) is calculated as follows:

$$\%\ R = \frac{|\ C_s - C\ |}{s} \times 100$$

where C_s equals the determined concentration (ng/ml) of the spiked aliquot, C equals the determined concentration (ng/ml), and s equals the concentration (ng/ml) of the spike added.

17.11.1 Every batch of 40 or less samples must include a low and a high spike.

17.11.2 A low spike should be at a concentration greater than the limit of quantitation (LOQ) and less than 10 times the LOD for each analyte to be reported.

17.11.3 A high spike should be at a concentration greater than 10 times the LOD for each analyte to be reported.

17.11.4 For method development, run test spikes of varying concentrations, from low to high, using in the ambient sample matrix.

17.11.5 For special project method testing, or where there is limited ambient sample available, sacrifice an ambient sample for testing and subsequent spiking (method confirmation) to provide a record of the reliability of the analysis method.

17.11.6 If the spike is not recovered within the specified limits, consider that the sample may be out of the linear range after spiking. If the out-of-limits

spike concentration remains in the linear range, this may indicate an under or over correction of an interference.

17.11.7 When checking for a matrix effect correction using a dilution, the results must agree within 10% of the original determination.

18. INSTRUMENTATION SCHEMATICS

18.1 ICP-MS

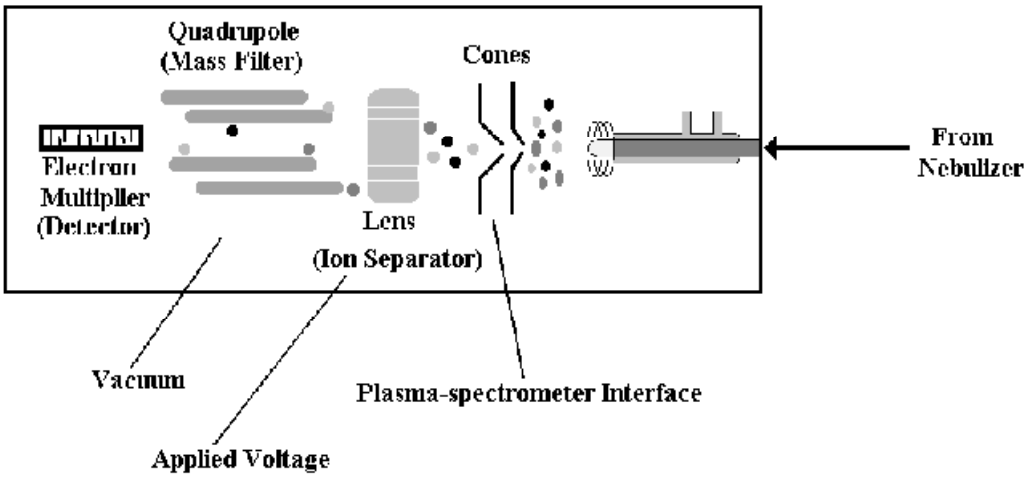

Figure 18.1, Perkin-Elmer ELAN 6100

18.2 ULTRASONIC NEBULIZER

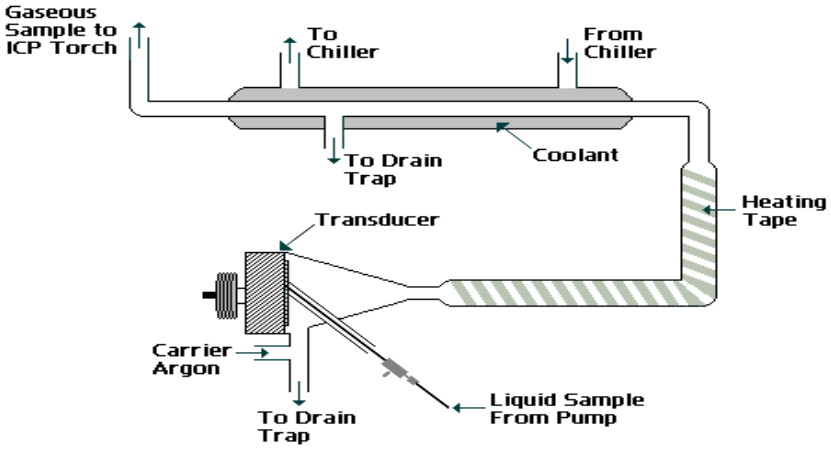

Figure 18.2, Ultrasonic Nebulizer

19. DAILY INSTRUMENT MAINTENANCE

-Check sample waste container level.
-Inspect argon tank supply.
-Check argon pressure to the instrument.
-Inspect chiller connections for possible leaks.
-Check vent system for blocks.
-Inspect torch and aerosol injector tubes.
-Inspect nebulizer for clogs.
-Inspect sample capillary tubing to be sure it is clean and good condition.
-Check peristaltic pump tubing before operation and every 3 hours of use (replace after 8 hours).
-At end of day, flush system for 5 minutes with the plasma on with a maximum of 2% nitric acid, followed by deionized water.

20. PERIODIC INSTRUMENT CHECKS

-Clean torch components and replace any worn O-rings on the torch assembly.
-Inspect and clean RF coil.
-Check nebulizer spray pattern; clean and replace tip as necessary.
-Clean nebulizer components and replace worn O-ring on the transducer face.
-Check drain fitting for leaks.
-Check that pump rollers are clean; remove and clean pump head as necessary.

21. HANDLING AND DISPOSAL OF ICP-MS CHEMICALS

The ICP-MS analyst is responsible for ensuring the safe storage and disposal of all chemical standards and reagents associated with this method.

21.1 Ordering Chemicals

21.1.1 Storage of excess chemicals takes up valuable lab space. Prior to ordering chemicals, assess needs carefully. Order only amounts that will be utilized within the following year.

21.1.2 Purchase smaller volumes whenever possible to minimize disposal costs of unused portions.

21.2 Disposing of Chemicals

21.2.1 The ICP-MS analyst is responsible for notifying the Division's Hazardous Waste Coordinator of disposal needs.

21.2.2 For disposal of the ICP-MS chemicals, the Hazardous Waste Coordinator should have the waste removal vendor do an inventoried lab-pack in favor of a drum. Drums of mixed chemicals are more difficult to profile

and create more problems to dispose of than lab-packs. Also, the chemicals can be stored as "usable materials" rather than "laboratory waste."

21.2.3 The autosampler rinse solution is less than 1% acidified DI water and can be disposed of in the laboratory sink, followed by a minute of flushing with tap water.

21.2.4 Standard dilutions in the parts-per-billion (ppb) range, which is the typical operating range of the ICP-MS, can be disposed of in the laboratory sink, followed by a minute of flushing with tap water. The exception is mercury (Hg) dilutions, which must be collected by the analyst and disposed of by the waste vendor.

21.2.5 The ICP-MS analyst is responsible for keeping chemicals and reagents separate and in their original containers.

22. REVISION HISTORY OF METHOD 061

REVISION	EFFECTIVE DATE	PRIMARY CHANGE(S) FROM PREVIOUS REVISION
MLD061, Draft	08/01/00	Startup of NLB trace metal analysis of low-volume ambient filter samples using ICP-MS; developed from U.S. EPA Method 6020 (9/94)
MLD061, Revision 0.0	01/01/02	Extraction procedure changed to eliminate use of ethanol, a contributor to numerous carbon-bonded interferences. Changed optimization and tuning procedures and solutions to accommodate instrument malfunctions and failures.

23. REFERENCES

1. Perkin-Elmer / SCIEX, "Elan 6100 Software Guide," November 1999.

2. EPA 600/R-94-111 Method 200.8, Trace Elements in Water and Wastes – ICP/MS, May 1994.

3. EPA SW-846 Ch 3.3 Method 6020, Metals by Inductively Couple Plasma/Mass Spectrometry, August 1994.

Table 1. OPTIMIZATION PROCEDURES

Procedure	When to Perform
X-Y Adjustment	Daily; whenever the cones are cleaned or replaced; or after any maintenance procedures in the torch chamber.
Nebulizer Gas Flow	Daily
Lens Voltage Optimization	Daily
Instrument Performance Check	Daily
Detector Optimization: Analog Stage Voltage Pulse Stage Voltage	Perform a Dual Detector Calibration when you require extended dynamic range (above two million counts per second) in a quantitative analysis. A detector calibration is always necessary if the Dual Mode in the method is selected.
Dead Time Correction	This procedure is only required when the detector is replaced, in which case, it should be performed after the detector optimization.
Dual Detector Calibration	Perform a Dual Detector Calibration when you require extended dynamic range (above two million counts per second) in a quantitative analysis. A detector calibration is always necessary if the Dual Mode in the method is selected. You must calibrate for each analyte. A minimum of two masses is required for a Dual Detector calibration.
Auto Lens Calibration	This is required when Auto Lens is used in the method. Also perform an Auto Lens calibration when sample matrices are significantly different to achieve the best performance with Auto Lens.

Table 2. QUALITY CONTROL PROCEDURES

Quality Control Procedure	Typical Frequency	Acceptance Criteria
Initial calibration (Section 9.1)	At the beginning of the analysis; must be done after tuning and optimization	Correlation coefficient, r2, must be > 0.9995, using a minimum of 3 standards and a reagent blank
Initial calibration verification Using the middle calibration standard (Section 17.5)	Analyzed immediately after the initial calibration	90%-110% of the actual concentration for all analytes to be determined
Initial calibration verification using the control standard (Section 9.2)	Analyzed immediately after running the calibration verification standards	90%-110% of the actual concentration for all analytes to be determined
Interference check standard (Section 9.10)	Analyzed as part of the method development process, whenever samples from a new site are added, or as a troubleshooting mechanism as findings warrant	90%-110% of the actual concentration for all analytes to be determined
Reagent Blank (Section 10.1)	Analyzed after calibration verifications, as a sample solution (pre-analysis); analyzed again, as a sample solution, at the end of each batch (post-analysis)	< LOD for all analytes to be reported; indicates contamination acquired during analysis
Continuing calibration Verification (Section 17.5)	Analyzed before the first Sample, after every 10 samples, and at the end of the run	90%-110% of the actual concentration for all analytes to be determined
Filter blanks (Section 10.3)	Random checks at intervals determined by analyst; analyzed as a sample	Document results of analytes reported to create historical record
Spike, low; at a concentration < 10 times the LOD (Section 17.11)	1 per sample set of 40 samples prepared using an aliquot of ambient sample; analyzed as a sample	80%-120% recovery for all analytes to be reported
Spike, high; at a concentration > 10 times the LOD (Section 17.11)	1 per sample set of 40 samples prepared using an aliquot of ambient sample; analyzed as a sample	80%-120% recovery for all analytes to be reported
Duplicate aliquot of sample solution (Section 17.9)	1 duplicate analyzed for every ten samples; analyzed as a sample	< 30% relative difference (%RD) for all analytes > LOQ

Table 3. OPERATING CONDITIONS FOR ICP-MS (WITH ULTRASONIC NEBULIZER)

Parameter	Operating Condition	Normal Range
Detector	Dual; Pulse/Analog	Dual; Pulse / Analog
Mode	Peak Hopping	Scanning / Peak Hopping
ICP RF Plasma	860 – 1250 W	800-1500 W
Nebulizer argon flow	0.6 – 0.7 L/min	0.5 – 0.95 L/min

Table 4. OPERATING CONDITIONS FOR ULTRASONIC NEBULIZER

Parameter	Operating Condition	Normal Range
Injector gas flow	0.6 L/min	0.3 – 1.5 L/min
Sample uptake	2.5 ml/min	0.1 – 3.0 ml/min
Heating temperature, nebulizer	140 ^{o}C	140 – 160 ^{o}C
Cooling temperature, nebulizer	3 ^{o}C	-5 – 10 ^{o}C
Heating temperature, desolvator	160 ^{o}C	120 – 160 ^{o}C
Sweep gas flow	2.0 L/min	1.4 –2.4 L/min

Table 5. INTERFERENCE CRITERIA (BY ORDER)

Order	Possible Interference(s)	Check
1	Argides	Check at –40 mass for carrier, (Cl, C, N, etc.)
2	Oxides	Check at –16 mass for carrier (Mo, Ti, Ca, Zn, etc.)
3	Dioxides	Check at –32 mass for carrier
4	Doubly Charged Ions	Show at ½ original mass, i.e., shows at 69 for Ba-138.
5	Dimers	Show at double the original mass; typical dimers include N, Ar, S.
6	Hydrides	Check at –1 mass and at –17 mass for possible problems.
7	Nitrogen	Check at –14 mass for carrier

Table 6. SOME INTERFERENCE CONSIDERATIONS FOR AIR SAMPLES

Element	Interference(s)
Background	Background will contain numerous Argides (ArX); Ar-40, ArH, ArO, ArN, Ar_2O_2, N_2, CO, CO_2
Addition of organic solvents, e.g. C_2H_2OH	Increases overall Oxides, Dioxides, and Hydrides, especially CO, CO_2.
^{52}Cr	$^{40}Ar\ ^{12}C$
^{54}Cr	^{54}Fe
B	Contaminates glassware.
^{69}Ga	Do not use as Internal Standard if ^{138}Ba is present because of dimer interference. Use ^{71}Ga instead.
^{56}Fe	$^{40}Ar^{16}O$
^{45}Sc	Interferences: SiO, CO_2. Do not use ^{45}Sc as an Internal Standard for samples with high Si, or samples collected on quartz/glass fiber filters, or samples with high C.
^{28}Si	Difficult when using a nitric acid extraction because of N_2. Also, ICP torch is made of quartz. Si is not recommended by ICP-MS.
^{75}As	Interference: $^{40}Ar\ ^{35}Cl$ Do not add correction unless actually interferes; check low spike results.
^{58}Ni	ArO, NaCl
^{120}Sn	Preferred isotope.
^{64}Zn	S_2, $^{48}Ca^{16}O$